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⑸ Preparation of metallocene catalysts for polymerization of olefins.

⑸ This invention uses a new method of producing ionic metallocene compounds. These compounds are useful as catalysts for polymerization of olefins, primarily propylene. This method uses an ionizing agent which ionizes the neutral metallocene compound. The ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation. The anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation. One such compound is triphenylcarbenium tetrakis(pentafluorophenyl)boronate.

The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IV metallocene derivative.

EP 0 426 637 A2

## PREPARATION OF METALLOCENE CATALYSTS FOR POLYMERIZATION OF OLEFINS

## SPECIFICATION

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## BACKGROUND OF THE INVENTION

## 10 FIELD OF THE INVENTION:

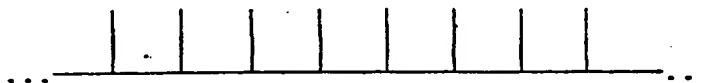
This invention relates, in general, to a process for preparing catalysts and, specifically, to a process for preparing catalysts for polymerization of olefins.

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## DESCRIPTION OF RELATED ART:

Olefins, especially propylene, may be polymerized to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as

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Isotactic polypropylene is capable of being a highly crystalline polymer with a high melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

A syndiotactic polymer contains principally units of exactly alternating stereoisomers and is represented by the structure:

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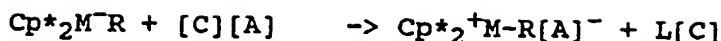
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A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

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Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that Zeigler-Natta catalysts for olefin polymerization can be formed by combining a group IV metallocene with an ionic compound.

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L

10 Cp\* - pentamethylcyclopentadienyl

M - Group IV metal

R - alkyl

15 L - ligand

[C] - cation

[A] - anion

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The resulting compound is a metallocene cation which acts as a catalyst. The cation [C] of the ionic compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

25 The following methods have been used to produce the above reaction:

One-Electron Oxidation - This method is illustrated in "Ethylene Polymerization by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, C.S. Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and [BPh<sub>4</sub>]<sup>-</sup> was the anion where Ph is C<sub>6</sub>H<sub>5</sub>. The reaction occurred in a coordinating solvent. These catalysts were usually of low activity.

30 Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis-(cyclopentadienyl)titanium Complexes", M. Bochmann, L.M. Wilson, J. Chem. Soc. Commun., p. 1610-1611, (1986); "Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes, M. Bochmann, L. Wilson, Organometallics, p. 1147-1154, Vol. 7 (1987).

35 European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:

40 bis(cyclopentadienyl)hafnium dimethyl + N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) cobaltate(III) → [Cp<sub>2</sub>HfMe][B] + CH<sub>4</sub> + N,N-dimethylaniline  
where [B] is 7,8-dicarbaundecaborane.

European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:

45 tri(n-butyl)ammonium tetra(pentafluorophenyl)boron + bis(cyclopentadienyl)zirconium dimethyl → [Cp<sub>2</sub>ZrMe][BPh<sub>4</sub>] + CH<sub>4</sub> + tri(n-butyl)N

50 A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating particular amines which are catalyst poisons. In addition, the catalyst and the polymer produced with this catalyst contains undesirable and toxic residual amines.

Ligand abstraction - The ligand abstraction method is illustrated in "Multiple Metal-Carbon Bonds", R. R. Schrock, P. R. Sharp, J. Am. Chem. Soc., p.2389-2399, Vol. 100, No. 8 (April, 2, 1978).

55 In most known processes, methylaluminoxane (MAO) is added with the metallocene compound to act as a cocatalyst. The function of MAO is to initiate the alkylation and promote ionization of the metallocene compound. The cocatalyst is a scavenging agent which reduces the poisons which decrease catalyst activity. Present known processes require a large excess of MAO to be added. MAO has the disadvantage

of being relatively expensive. This results in high costs for the catalyst system.

## SUMMARY OF THE INVENTION

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Accordingly, it is an object of this invention to provide a process for making an improved catalyst for polymerization of olefins.

And, it is an object of this invention to provide a process for making a catalyst with relatively high activity.

Also, it is an object of this invention to synthesize metallocene cations with no Lewis base as a side product.

Further, it is an object of this invention to eliminate the necessity to chose starting materials to control the by-products which may be produced as catalyst poisons.

Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerization of polypropylene.

Moreover, it is an object of this invention to produce polymers which are free of aluminum oxide.

As well, it is an object of this invention to produce a polymer which is free of undesirable and toxic amines.

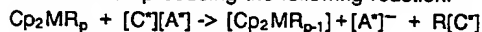
These and other objects are accomplished by mixing an ionizing agent, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, with derivatives of metallocenes and adding the mixture to an olefin.

## DESCRIPTION OF THE INVENTION

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The invention is for a process of producing a catalyst for polymerization of olefins by ionizing a metallocene with an ionizing agent which does not contain an active proton and which has an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene. The anion is also chemically unreactive with the cation.

In the new synthesis procedure the ionizing ionic compound is mixed with neutral derivatives of metallocenes producing the following reaction:

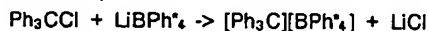


where Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except that if R is a hydride only one R is a hydride, p is from 1 to 4, C<sup>+</sup> is a carbonium, oxonium or sulfonium cation and A<sup>-</sup> is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and is chemically unreactive with [Cp<sub>2</sub>MR<sub>p-1</sub>].

Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation. Examples of such solvents are toluene and methylene chloride. The preferred solvent is toluene. The two reactants are dissolved separately in the same solvent and are mixed together at room temperature at a mole ratio ranging from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound. A preferred mole ratio is from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound. The most preferred mole ratio is 1 mole of metallocene : 1 mole of ionizing compound. After mixing, the mixture is added to an olefin under conditions to effect polymerization. The preferred olefins are ethylene and propylene, the most preferred being propylene.

An ionic compound containing a carbonium, oxonium or sulfonium ion, such as triphenylcarbenium tetrakis(pentafluorophenyl)boronate, is mixed with a neutral derivative of a metallocene. Triphenylcarbenium tetrakis(pentafluorophenyl)boronate acts as an ionizing agent which ionizes the metallocene. A cationic metallocene catalyst is formed.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate [Ph<sub>3</sub>C][BPh<sub>4</sub><sup>-</sup>] is produced by the following reaction:



where Ph is phenyl and Ph<sup>+</sup> is pentafluorophenyl. Triphenylcarbenium is a cation. Tetrakis(pentafluorophenyl) boronate is an anion.

Triphenylcarbenium tetrakis(pentafluorophenyl)boronate was produced with the following laboratory method. A bright yellow solution of 27.1 mmoles of Ph<sub>3</sub>CCl in 150 cc of methylene chloride was added

dropwise at 25°C to 25 gm of  $\text{LiB}(\text{C}_6\text{F}_5)_4$  slurried in 350 cc of methylene chloride. The orange slurry was stirred for 30 minutes and then filtered. The solids containing  $[\text{Ph}_3\text{C}][\text{BPh}_4]$  and  $\text{LiCl}$  were washed with methylene chloride. The combined wash and filtrate was concentrated to 75 cc and then cannulated into 400 cc of pentane with rapid stirring. The solids were washed several times with pentane and small amounts of toluene until a bright yellow powder of  $[\text{Ph}_3\text{C}][\text{BPh}_4]$  was obtained. The yield was 20 grams (75%).

The neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, preferably a Group IV metal, such as titanium, hafnium or zirconium, most preferably zirconium for higher catalyst activity and hafnium for higher molecular weight, R is a hydride, a halogen, an amide or a hydrocarbyl radical such as an alkyl, aryl, alkenyl, alkylaryl or arylalkyl radical having from 1 to 20 carbon atoms, each R being the same or different, except that if R is a hydride only one R is a hydride and p is from 1 to 4. The preferred neutral derivatives of metallocene are ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dimethyl. The most preferred neutral derivative of metallocene is ethylene bis(indenyl)zirconium dimethyl.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80°C to 150°C, preferably 25°C to 90°C and most preferably from 50°C to 80°C.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

#### EXAMPLE I

55 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 5 cc of toluene. 40 mg of  $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$  was dissolved in 5 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature, giving a clear yellow solution.

The mixture was added by syringe to a 2 liter Zipperclave reactor. 1.0 liter of propylene was added to the reactor. Reactor temperature was set to 70°C. The contents of the reactor were agitated. The temperature remained at 70°C during the sixty minute polymerization period after which propylene was vented from the reactor. The contents of the reactor were washed with acetone and dried in a vacuum oven.

The polymer was analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

#### EXAMPLE II

The procedure of Example I was repeated using 40 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 20 mg of  $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$ . The results are shown in Table I.

#### EXAMPLE III

The procedure of Example I was repeated using 30 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 15 mg of  $\text{Et}(\text{IndH}_4)_2\text{ZrMe}_2$ . The reactor temperature was set at 80°C and the temperature remained at 80°C. The results are shown in Table I.

#### EXAMPLE IV

The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of  $\text{Et(IndH}_4\text{)ZrMe}_2$ . Reactor temperature was set at 50°C and the temperature remained at 100°C. Run time was 10 minutes. The results are shown in Table I.

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## EXAMPLE V

The procedure of Example I was repeated using 55 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 50 mg of  $\text{Et(IndH}_4\text{)ZrMe}_2$ . Reactor temperature was set at 50°C and increased to 166°C. Run time was 10 minutes. The results are shown in Table I.

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## EXAMPLE VI

The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$ . Reactor temperature was set at 50°C and the temperature remained at 50°C. The results are shown in Table I.

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## EXAMPLE VII

The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$ . The temperature was set at 50°C and remained at 50°C. The results are shown in Table I.

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## EXAMPLE VIII

The procedure of Example I was repeated using 120 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 80 mg of  $\text{iPr(Cp-1-Flu)ZrMe}_2$ . Reactor temperature was set at 70°C and the temperature increased above 100°C. The results are shown in Table I.

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## EXAMPLE IX

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The procedure of Example I was repeated using 100 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 60 mg of  $\text{iPr(Cp-1-Flu)ZrMe}_2$ . Reactor temperature was set at 70°C and the temperature increased to 78°C. The results are shown in Table I.

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## EXAMPLE X

The procedure of Example I was repeated using 60 mg of triphenylcarbenium tetrakis-(pentafluorophenyl)boronate and 40 mg of  $\text{iPr(Cp-1-Flu)ZrMe}_2$ . Reactor temperature was set at 70°C. The results are shown in Table I.

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The following results are from the experimental runs described above using the method of the present invention.

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TABLE I

RUN #	CATALYST, + mg	IONIZING AGENT, + + mg	TIME, min.
	Et(IndH <sub>4</sub> ) <sub>2</sub> ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]	
1	40	55	60
2	20	40	60
3	15	30	80
4	50	60	10
5	50	55	10
	Et(Ind) <sub>2</sub> ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]	
6	60	100	60
7	60	100	30
	iPr(Cp-1-Flu)ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]	
8	80	120	5
9	60	100	60
10	40	60	60

+ Et(IndH<sub>4</sub>)<sub>2</sub>ZrMe<sub>2</sub> = Ethylenebis(tetrahydroindenyl)zirconium dimethyl  
 Et(Ind)<sub>2</sub>ZrMe<sub>2</sub> = Ethylenebis(indenyl)zirconium dimethyl  
 iPr(Cp-1-Flu)ZrMe<sub>2</sub> = isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl  
 + + [Ph<sub>3</sub>C][BPh<sub>4</sub>] = triphenylcarbenium tetrakis(pentafluorophenyl)boronate.

RUN #	TEMP, °C	YIELD, gm	Melting Temp °C
1	70	9	138
2	50	55	138
3	80	45	131
4	50*	74	134
5	50*	135	-
6	50	19	137
7	50	11	134
8	70*	224	115
9	70**	51	-
10	70***	186	119

\*Runaway reaction; peak reaction temperature &gt;100°C

\*\*Exotherm; peak reaction temperature 78°C

\*\*\*Exotherm

The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization. The process of making catalysts with this invention produces catalysts having high activity and does not produce by-products which can inhibit catalyst activity. This new synthesis is a clean reaction which does not produce a Lewis base. The process generates active catalysts by removing a methyl anion from a group IV metallocene derivative.

Obviously, numerous modifications and variations of the present invention are possible in light of the

above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

## 5 Claims

1. A process for making a catalyst comprising:

a) mixing an ionizing ionic compound with a neutral derivative of a metallocene; and

b) allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst;

wherein the neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

2. A process as recited in Claim 1 wherein, before mixing, the ionizing ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.

3. A process as recited in Claim 2 wherein, before mixing the neutral derivative of a metallocene is separately dissolved in the same solvent.

4. A process as recited in Claim 3 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.

5. A process as recited in Claim 4 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound.

6. A process as recited in Claim 5 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.

7. A process as recited in Claim 4 wherein the metal is a Group IV metal chosen from the group consisting of titanium, zirconium and hafnium.

8. A process as recited in Claim 7 wherein the metal is hafnium.

9. A process as recited in Claim 7 wherein the metal is zirconium.

10. A process as recited in Claim 9 wherein R is a hydrocarbyl radical chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.

11. A process as recited in Claim 10 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.

12. A process as recited in Claim 11 wherein the neutral derivative of a metallocene is ethylenebis(indenyl)zirconium dimethyl.

13. A process as recited in Claim 12 wherein the ionic compound is triphenylcarbenium tetrakis-(pentafluorophenyl) boronate.

14. A process as recited in Claim 13 wherein the solvent is toluene.

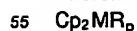
15. A process for polymerization of an olefin comprising:

a) mixing an ionizing ionic compound with a neutral derivative of a metallocene;

b) allowing contact between the ionizing ionic compound and the neutral derivative of a metallocene such that the metallocene is ionized by the ionizing ionic compound and an ion pair is formed in which the metallocene cation acts as a catalyst; and

c) contacting the catalyst with the olefin under conditions to effect polymerization;

wherein the neutral derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4;



wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

- 5 16. A process as recited in Claim 15 wherein, before mixing, the ionic compound is dissolved in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation.
17. A process as recited in Claim 16 wherein, before mixing, the neutral derivative of a metallocene is dissolved in the same solvent.
18. A process as recited in Claim 17 wherein the mole ratio of the neutral derivative of a metallocene to the  
10 ionic compound ranges from 10 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 10 moles of ionizing compound.
19. A process as recited in Claim 18 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges from 2 moles of metallocene : 1 mole of ionizing compound to 1 mole of metallocene : 2 moles of ionizing compound.
- 15 20. A process as recited in Claim 19 wherein the mole ratio of the neutral derivative of a metallocene to the ionic compound ranges is 1 mole of metallocene : 1 mole of ionizing compound.
21. A process as recited in Claim 18 wherein the metal is a Group IV metal chosen from the group consisting of titanium, zirconium and hafnium.
22. A process as recited in Claim 21 wherein the metal is hafnium.
- 20 23. A process as recited in Claim 21 wherein the metal is zirconium.
24. A process as recited in Claim 23 wherein R is a hydrocarbyl chosen from the group consisting of an alkyl radical, an aryl radical, an alkenyl radical, an alkylaryl radical and an arylalkyl radical having from 1 to 20 carbon atoms.
25. A process as recited in Claim 24 wherein the neutral derivative of a metallocene is chosen from the  
25 group consisting of ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
26. A process as recited in Claim 25 wherein the neutral derivative of a metallocene is ethylene bis-(indenyl)zirconium dimethyl.
27. A process as recited in Claim 26 wherein the ionic compound is triphenylcarbenium tetrakis-  
30 (pentafluorophenyl) boronate.
28. A process as recited in Claim 27 wherein the solvent is toluene.
29. A process as recited in Claim 28 beginning at a reaction temperature which ranges from -80°C to 150°C.
30. A process as recited in Claim 29 beginning at a reaction temperature which ranges from 25°C to 90°C.
- 35 31. A process as recited in Claim 30 beginning at a reaction temperature which ranges from 50°C to 80°C.

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## EUROPEAN PATENT APPLICATION

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54 **Metallocene catalysts with lewis acids and aluminum alkyls.**

57 This invention is for a catalyst system comprising a neutral metallocene compound, an aluminum alkyl and a Lewis acid. The Lewis acid must be of sufficient acidity to ionize a neutral metallocene compound to form a cationic metallocene catalyst. The ligands of the Lewis acid should not be reactive with the metallocene cation. Any metallocene catalyst compound having two cyclopentadienyl rings attached to a transition metal would be useful in this invention.

The invention is also for the process of using the catalyst system in polymerization of olefins. The metallocene is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

EP 0 427 697 A3



European  
Patent Office

## EUROPEAN SEARCH REPORT

Application Number

EP 90 87 0176

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 110, 1988, pages 1647-1649, American Chemical Society; D. HEDDEN et al.: "[ $(\text{CH}_3)_5\text{C}_5$ ]2Th( $\text{CH}_3$ ) <sub>2</sub> surface chemistry and catalysis. direct NMR spectroscopic observation of surface alkylation and ethylene insertion/polymerization on $\text{MgCl}_2$ " * Whole article * - - -	1	C 08 F 4/602 C 08 F 4/606 C 08 F 10/00
Y	JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 108, 1986, pages 7410-7411, American Chemical Society; R.F. JORDAN et al.: "Ethylene polymerization by a cationic dicyclopentadienylzirconium(IV) alkyl complex" * Whole article * - - -	1	
Y	MACROMOLECULES, 1989, pages 2186-2189, American Chemical Society; A. ZAMBELLI et al.: "Isotactic polymerization of propene: Homogeneous catalysts based on group 4 metallocenes without methylalumoxane" * Whole article * - - -	1	
Y	EP-A-0 277 004 (EXXON) * Claims * - - - - -	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C 08 F
The present search report has been drawn up for all claims			
Place of search  The Hague		Date of completion of search  13 May 91	Examiner  DE ROECK R.G.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &amp;: member of the same patent family, corresponding document</div>			

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(54) **Metallocene catalysts with lewis acids and aluminum alkyls.**

(57) This invention is for a catalyst system comprising a neutral metallocene compound, an aluminum alkyl and a Lewis acid. The Lewis acid must be of sufficient acidity to ionize a neutral metallocene compound to form a cationic metallocene catalyst. The ligands of the Lewis acid should not be reactive with the metallocene cation. Any metallocene catalyst compound having two cyclopentadienyl rings attached to a transition metal would be useful in this invention.

The invention is also for the process of using the catalyst system in polymerization of olefins. The metallocene is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

**EP 0 427 697 A2**

## METALLOCENE CATALYSTS WITH LEWIS ACIDS AND ALUMINUM ALKYL

## FIELD OF THE INVENTION:

This invention relates, in general, to an improved catalyst system and a process for using the improved catalyst system and, specifically, to a catalyst system of a metallocene compound with a Lewis acid and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins, primarily propylene.

## DESCRIPTION OF RELATED ART:

The use of metallocene compounds as catalysts for the polymerization of olefins is known. German patent application No. 2,608,863 discloses a catalyst system for the polymerization of ethylene consisting of bis(cyclopentadienyl)titanium dialkyl, an aluminum trialkyl and water. German patent application No. 2,608,933 discloses an ethylene polymerization catalyst system consisting of zirconium metallocenes of the general formula (cyclopentadienyl)<sub>n</sub>ZrY<sub>4-n</sub>, wherein Y represents R<sub>1</sub>CH<sub>2</sub>AlR<sub>2</sub>, CH<sub>2</sub>CH<sub>2</sub>AlR<sub>2</sub> and CH<sub>2</sub>CH(AlR<sub>2</sub>)<sub>2</sub> where R stands for an alkyl or metallo alkyl, and n is a number within the range 1-4; and the metallocene catalyst is used in combination with an aluminum trialkyl cocatalyst and water.

The use of metallocenes as catalysts in the copolymerization of ethylene and other alpha-olefins is also known in the art. U.S. Pat. No. 4,542,199 to Kaminsky, et al. discloses a process for the polymerization of olefins and particularly for the preparation of polyethylene and copolymers of polyethylene and other alpha-olefins. The disclosed catalyst system includes a catalyst of the formula (cyclopentadienyl)<sub>2</sub>MeRHal in which R is a halogen, a cyclopentadienyl or a C<sub>1</sub>-C<sub>6</sub> alkyl radical, Me is a transition metal, in particular zirconium, and Hal is a halogen, in particular chlorine. The catalyst system also includes an alumoxane having the general formula Al<sub>2</sub>OR<sub>4</sub>(Al(R)-O)<sub>n</sub> for a linear molecule and/or (Al(R)-O)<sub>n+2</sub> for a cyclic molecule in which n is a number from 4-20 and R is a methyl or ethyl radical. A similar catalyst system is disclosed in U.S. Pat. No. 4,404,344.

U.S. Pat. No. 4,530,914 discloses a catalyst system for the polymerization of ethylene to polyethylene having a broad molecular weight distribution and especially a bimodal or multimodal molecular weight distribution. The catalyst system is comprised of at least two different metallocenes and an alumoxane. The patent discloses metallocenes that may have a bridge between two cyclopentadienyl rings with the bridge serving to make those rings stereorigid.

European Patent Publication No. 0185918 discloses a stereorigid, chiral zirconium metallocene catalyst for the polymerization of olefins. The application does not indicate that hafnium could be substituted for the zirconium and used to produce a useful polymer product. The bridge between the cyclopentadienyl groups is disclosed as being a linear hydrocarbon with 1-4 carbon atoms or a cyclical hydrocarbon with 3-6 carbon atoms.

Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane (MAO) as a cocatalyst. A system for the production of isotactic polypropylene using a titanium or zirconium metallocene catalyst and an alumoxane cocatalyst is described in "Mechanisms of Stereochemical Control in Propylene Polymerization with Soluble Group 4B Metallocene/Methylaluminoxane Catalysts," J. Am. Chem. Soc., Vol. 106, pp. 6355-64, 1984. The article shows that chiral catalysts derived from the racemic enantiomers of ethylene-bridged indenyl derivatives form isotactic polypropylene by the conventional structure predicted by an enantiomeric-site stereochemical control model. The meso achiral form of the ethylene-bridged titanium indenyl diastereomers and achiral zirconocene derivatives, however, produce polypropylene with a purely atactic structure.

MAO activates the metallocene which then becomes able to promote polymerization of alpha-olefins. Other organometallic compounds of aluminum, such as trimethylaluminum (TMA) or dimethyl aluminum halide, are known not to promote polymerization by themselves. Neither aluminum alkyls nor dimethylaluminum halides alone are active cocatalysts.

A combination of TMA and dimethylaluminum fluoride (DMF) has been shown to be effective as a cocatalyst in place of MAO. DMF is a Lewis acid. Such a combination is reported in "Isotactic Polymerization of Propene: Homogeneous Catalysts Based on Group 4 Metallocenes without Methylaluminoxane", A. Zambelli, P. Longo and A. Grassi, Macromolecules, Vol. 22, p. 2186-2189, 1989. The stereochemical

structure of the polymers prepared with TMA/DMF and with MAO were very similar. However, the polymerization yields obtained for TMA/DMF mixtures were substantially lower than those obtained for MAO.

It has also been reported that a metallocene compound with magnesium chloride forms a catalyst system with bis(cyclopentadienyl)thorium dimethyl which is effective to polymerize ethylene. Such a combination is reported in "[ $(CH_3)_5C_5$ ] $_2Th(CH_3)_2$  Surface Chemistry and Catalysis. Direct NMR Spectroscopic Observation of Surface Alkylation and Ethylene Insertion/Polymerization on  $MgCl_2$ ". D. Heddin and T. J. Marks, J. Am. Chem. Soc., Vol. 110, No.5, 1988. A methyl group is abstracted from the cyclopentadienyl compound and a cation is formed. The methyl group coordinates with the magnesium to form a magnesium anion. Magnesium chloride is a Lewis acid.

Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent, such as methylaluminoxane. Polymerization requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

## SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a catalyst system of a metallocene compound with a Lewis acid and an aluminum alkyl and a process for using the improved catalyst system for polymerization of olefins. Homopolymers or copolymers produced by the polymerization of alpha olefins may be produced in accordance with the present invention. Propagation of the polymer chain is carried out in the presence of a neutral alkyl derivative of a metallocene compound which has been put into contact with a Lewis acid and an aluminum alkyl. Any metallocene catalyst compound having two cyclopentadienyl rings coordinated to a transition metal would be useful in this invention.

The catalyst is contacted with the Lewis acid. The aluminum alkyl is contacted with the olefin. The two mixtures are contacted with each other under polymerization conditions.

## DESCRIPTION OF THE INVENTION

This invention is for a catalyst system comprising a metallocene catalyst, a Lewis acid and an aluminum alkyl and a process for using the catalyst system for polymerization of olefins.

The metallocene catalyst is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, halogen, amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4. M is preferably a Group IV metal such as titanium, zirconium or hafnium and is most preferably zirconium. R is preferably an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms. R is most preferably an alkyl or alkoxy up to six carbons atoms or an aryl up to 10 carbon atoms. The neutral derivative of the metallocene is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl or ethylene bis(indenyl)zirconium dimethyl and is most preferably ethylene bis(indenyl)zirconium dimethyl.

The Lewis acid useful in this invention is any material which can accept an electron pair and is of sufficient acidity to ionize a neutral metallocene to form a cationic metallocene catalyst. In addition, the ligands of the Lewis acid cannot be reactive with the metallocene cation. Preferably, the Lewis acid contains boron or is magnesium chloride ( $MgCl_2$ ). Most preferably, the Lewis acid is tris(pentafluorophenyl)boron.

The aluminum alkyl is of the general formula  $AlR_3$  where R is halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl. Preferably, the aluminum alkyl is trimethyl aluminum (TMA) or triethyl aluminum (TEAL). Most preferably, the aluminum alkyl is triethyl aluminum.

In the practice of this invention, the aluminum alkyl is mixed with the olefin. The Lewis acid is dissolved or slurried in a nonpolar solvent. The neutral metallocene catalyst is dissolved separately in the same solvent. The Lewis acid mixture and the catalyst mixture are combined. The mixture is placed in contact with the blend of olefin and aluminum alkyl. Molar ratios for metallocene:Lewis acid:aluminum alkyl range from 0.01:1:0.1 to 5:1:350 and are preferably from 0.5:1:0.5 to 4:1:25 and are most preferably 0.02:1:1 for Lewis acids which dissolve in a nonpolar solvent and 0.01:1:1 for Lewis acids which form a slurry in

nonpolar solvents.

Polymerization of the olefin is accomplished by any of the known means for polymerization of olefins with metallocene catalysts, for example polymerization in bulk, slurry or gas phase. For polypropylene, polymerization temperatures range from -80 °C to 150 °C, preferably 25 °C to 90 °C and most preferably from 50 °C to 80 °C.

The following catalyst system were evaluated with and without addition of an aluminum alkyl and with and without addition of a Lewis acid.

1.  $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2/\text{F15}/\text{TEAl}$  (TMA)
2.  $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2/\text{MgCl}_2/\text{TEAl}$
3.  $\text{Et}(\text{Ind})_2\text{ZrMe}_2/\text{F-15}/\text{TEAl}$
4.  $\text{Et}(\text{Ind})_2\text{ZrMe}_2/\text{MgCl}_2/\text{TEAl}$

$\text{Et}(\text{Ind})_2\text{ZrMe}_2$  is ethylenebis(indenyl)zirconium dimethyl,  $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$  is isopropylidene (cyclopentadienyl 1-fluorenyl)zirconium dimethyl and F15 is tris(pentafluorophenyl)boron.

A combination of aluminum alkyl and a Lewis acid was found to be necessary for reproducible, controllable, high efficiency polymerizations.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

#### GROUP 1:

#### EXAMPLE I

0.16 mmol of triethylaluminum (TEAl) Was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70 °C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

35 mg of  $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$  was dissolved in 10 ml of toluene. The catalyst was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70 °C and the contents of the reactor were agitated for thirty minutes. At the end of the polymerization, the reactor was cooled and the unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

#### EXAMPLE II

0.33 mmol of triethylaluminum (TEAl) was dissolved in 5 ml of toluene and added to a Zipperclave reactor. Reactor temperature was set to 70 °C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for 15 minutes at 1200 rpm.

78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 60 mg of  $i\text{Pr}(\text{Cp-I-Flu})\text{ZrMe}_2$  was dissolved in 10 cc of toluene to form a yellow solution. The two solutions were mixed together and formed a red solution which was mixed for 5 minutes at room temperature.

The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. The reactor temperature increased to 90 °C. Unreacted propylene was vented from the reactor and the reaction product was washed with acetone and dried in a vacuum.

The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

#### EXAMPLE III

The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAl), 27 mg of tris-(pentafluorophenyl)boron and 20 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE IV

The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAl), 46 mg of tris-(pentafluorophenyl)boron and 15 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE V

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The procedure of Example II was repeated using 0.10 mmol of triethyl aluminum (TEAl), 46 mg of tris-(pentafluorophenyl)boron and 35 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE VI

The procedure of Example II was repeated using 0.16 mmol of triethyl aluminum (TEAl), 46 mg of tris-(pentafluorophenyl)boron and 35 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE VII

The procedure of Example II was repeated using 0.33 mmol of triethyl aluminum (TEAl), 46 mg of tris-(pentafluorophenyl)boron and 35 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor. There was no reaction product. The results are shown in Table I.

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## EXAMPLE VIII

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The procedure of Example II was repeated using 0.16 mmol of trimethyl aluminum (TMA), 46 mg of tris-(pentafluorophenyl)boron and 35 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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Group 2:

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## EXAMPLE IX

0.16 mmol of triethyl aluminum (TEAl) was dissolved in 5 ml of toluene and was added to a 2 liter zipperclave reactor under 5 psig of nitrogen.

Reactor temperature was set at 60 °C and 1 liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

86 mg of  $\text{MgCl}_2$  was slurried in 5 cc of toluene. 18 mg of  $i\text{Pr}(\text{Cp-}i\text{Flu})\text{ZrMe}_2$  was cannulated into the  $\text{MgCl}_2$  slurry. The mixture was stirred for 12 hours to give a dark purple suspension.



The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The contents of the reactor were agitated for thirty minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with a dilute HCl methanol solution and dried in a vacuum oven.

- 5 The polymer was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

10 Group 3:

#### EXAMPLE X

- 15 One liter of propylene was added to the Zipperclave reactor. Reactor temperature was set to 70 °C. 78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene. 58 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$  was dissolved in 18 cc of toluene. The two solutions were mixed together for 5 minutes at room temperature.

- 20 The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature was maintained at 70 °C and the contents of the reactor were agitated for 35 minutes. Unreacted propylene was vented from reactor. There was no reaction product. The results are shown in Table I.

#### EXAMPLE XI

- 25 0.33 mmol of triethylaluminum (TEAL) was dissolved in 5 ml of non coordinating solvent and added to a Zipperclave reactor. Reactor set point temperature was set to 70 °C and 1.0 liter of propylene was added to the reactor. The mixture was stirred for ten minutes at 1200 rpm.

- 30 78.6 mg of tris(pentafluorophenyl)boron was dissolved in 5 cc of toluene to form a colorless solution. 58 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$  was dissolved in 10 cc of toluene to form a pale yellow solution. The two solutions were mixed together to form a clear dark yellow solution which was mixed for 5 minutes at room temperature.

- 35 The catalyst mixture was added to a 50 ml stainless steel bomb. 200 ml of propylene was pumped through the bomb into the reactor. The reactor temperature increased to over 95 °C and the contents of the reactor were agitated for six minutes. Unreacted propylene was vented from the reactor and the reaction product was washed with acetone and dried in a vacuum.

- 40 The polypropylene reaction product was analyzed for melting point and molecular weight. The melting point was derived from differential scanning calorimetry (DCS). The molecular weight was calculated using gel permeation chromatography (GPC) analysis. The results are shown in Table I.

#### EXAMPLE XII

- 45 The procedure of Example XI was repeated using 0.66 mmol of TEAL, 27 mg of tris(pentafluorophenyl)boron and 20 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$ . The contents of the reactor were agitated for 22 minutes. The results are shown in Table I.

#### EXAMPLE XIII

- 55 The procedure of Example XI was repeated using 0.33 mmol of TEAL, 2.5 mg of tris(pentafluorophenyl)boron and 2.5 mg of  $\text{Et(Ind)}_2\text{ZrMe}_2$ . The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XIV

5 The procedure of Example XI was repeated using 0.66 mmol of TEAl, 102 mg of tris-(pentafluorophenyl)boron and 2.5 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

EXAMPLE XV

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The procedure of Example XI was repeated using 0.66 mmol of TEAl, 154 mg of tris-(pentafluorophenyl)boron and 2.5 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

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EXAMPLE XVI

20 The procedure of Example XI was repeated using 0.66 mmol of TEAl, 308 mg of tris-(pentafluorophenyl)boron and 2.5 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for 30 minutes. The results are shown in Table I.

25 Group 4:

EXAMPLE XVII

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The procedure of Example IX was repeated with 352 mg of magnesium chloride, 40 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

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EXAMPLE XVIII

The procedure of Example IX was repeated with 352 mg of magnesium chloride, 10 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

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EXAMPLE XIX

45 The procedure of Example IX was repeated with 124 mg of magnesium chloride, 40 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>, 0.66 mmol of TEAl and a run time of thirty minutes. The results are shown in Table I.

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Run #	Catalyst $\mu\text{mol}$ (mg)	Lewis Acid $\mu\text{mol}$ (mg)	Aluminum Alkyl mmol	Run Time min
1.	iPr(Flu)(Cp)ZrMe <sub>2</sub>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	TEA1	
2.	89.8(35)	0	0.16	30
3.	153(60)	153 (78.6)	0.33	30
4.	51.2(20)	52.73(27)	0.33	30
5.	38.4(15)	89.8(46)	0.16	30
6.	89.5(35)	89.8(46)	0.10	30
7.	89.5(35)	89.8(46)	0.16	30
8.	89.5(35)	89.8(46)	0.33	30
9.	89.5(35)	89.8(46)	TMA 0.16	30
10.	45(18)	MgCl <sub>2</sub> 900(86)	TEAL 0.66	30
11.	Et(Ind) <sub>2</sub> ZrMe <sub>2</sub> 154(58)	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> 154(78.6)	0	35
12.	154(58)	154(78.6)	0.33	6
13.	53(20)	53(27)	0.66	22
14.	6.6(2.5)	6.6(2.5)	0.33	30
15.	6.6(2.5)	200(102)	0.66	30
16.	6.6(2.5)	300(154)	0.66	30
17.	6.6(2.5)	600(308)	0.66	30
18.	Et(Ind)ZrMe <sub>2</sub> 106(40)	MgCl <sub>2</sub> 3700(352)	TEA1 0.66	30
19.	27(10)	3700(352)	0.66	30
	106(40)	1300(124)	0.66	30

Run #	Polymerization Temp °C	Yield	Melting Temp °C	Molecular Weight x 1000	Molecular Weight Distribution
1.	70	0	-	-	-
2.	70	123	-	57.6	1.9
3.	70	7	110	64.3	2.0
4.	70	58	-	-	-
5.	70	5	105	39	2.0
6.	70	168	105	61	1.9
7.	70	110	123	55	2.0
8.	70	167	-	-	-
9.	60	6	131	57	2.0
10.	70	0	-	-	-
11.	70	117	113	15	4.2
12.	70	70	122	17.5	3.5
13.	70	0	-	-	-
14.	70	1	127	26	2.8
15.	70	90	130	20	5.1
16.	70	33	129	25	3.7
17.	70	49	133	31	1.9
18.	70	47	130	29	2.4
19.	70	8	130	30	2.0

For the F15 catalyst system, higher efficiencies were obtained by increasing the B:Zr molar ratio significantly above 1:1. This implies that the lower efficiencies are partly due to incomplete ionization by F15.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings.

It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

# Claims

1. A catalyst system comprising:
  - a) a neutral metallocene compound;
  - b) an aluminum alkyl; and
  - c) a Lewis acid;
 wherein the aluminum alkyl is of the general formula  $AlR_3$  where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl,
- wherein the neutral metallocene compound is of the general formula:  $Cp_2MR_p$ 
 wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the same or different, except only one R is a hydride and p is from 1 to 4,
- wherein the Lewis acid is of sufficient acidity to ionize a neutral metallocene compound to form a cationic metallocene catalyst, and
 wherein the ligands of the Lewis acid are not reactive with the metallocene cation.
2. A catalyst as recited in Claim 1 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
3. A catalyst as recited in Claim 2 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
4. A catalyst as recited in Claim 1 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
5. A catalyst as recited in Claim 4 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene(cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
6. A catalyst as recited in Claim 1 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
7. A catalyst as recited in Claim 6 wherein the aluminum alkyl is triethylaluminum.
8. A catalyst as recited in Claim 1 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
9. A catalyst as recited in Claim 8 wherein the Lewis acid is tris(pentafluorophenyl)boron.
10. A process for preparing a catalyst comprising:
  - a) mixing a Lewis acid with a neutral metallocene compound; and
  - b) allowing contact between the ionizing ionic compound and the neutral metallocene compound;
 wherein the neutral derivative of a metallocene is of the general formula:  $Cp_2MR_p$ 
 wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical,
- each R being the same or different, except only one R is a hydride and p is from 1 to 4;
11. A process as recited in Claim 10 wherein the olefin is propylene.
12. A process as recited in Claim 10 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
13. A process as recited in Claim 10 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
14. A process as recited in Claim 13 wherein the M is zirconium.
15. A process as recited in Claim 14 wherein the neutral derivative of a metallocene is chosen from the group consisting of ethylenebis(indenyl)zirconium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
16. A process as recited in Claim 10 wherein the Lewis acid is chosen from the group consisting of all Lewis acids containing boron and magnesium chloride.
17. A catalyst as recited in Claim 16 wherein the Lewis acid is tris(pentafluorophenyl)boron.
18. A process for polymerization of olefins comprising:

- a) mixing an aluminum alkyl with an olefin;  
 b) mixing a neutral metallocene compound with a Lewis acid;  
 c) mixing the metallocene-Lewis acid mixture with the aluminum alkyl-olefin mixture.  
 wherein the aluminum alkyl is of the general formula  $AlR_3$  where R is a halogen, oxygen, hydride, alkyl,  
 5 alkoxy or aryl, each R being the same or different and at least one R is an alkyl; and  
 wherein the neutral metallocene compound is of the general formula:  
 $CP_2MR_p$   
 wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a  
 Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, each R being the  
 10 same or different, except only one R is a hydride and p is from 1 to 4.  
 19. A process as recited in Claim 18 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to  
 10 carbons.  
 20. A process as recited in Claim 19 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl  
 ranges from 0.01:1:0.1 to 5:1:350.  
 15 21. A process as recited in Claim 20 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl  
 ranges from 0.5:1:05 to 4:1:25.  
 22. A process as recited in Claim 21 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is  
 0.02:1:1.  
 23. A process as recited in Claim 21 wherein the molar ratio for metallocene:Lewis acid:aluminum alkyl is  
 20 0.01:1:1.  
 24. A process as recited in Claim 16 wherein the aluminum alkyl is selected from the group consisting of  
 triethylaluminum and trimethylaluminum.  
 22. A process as recited in Claim 21 wherein the aluminum alkyl is triethylaluminum.  
 23. A catalyst as recited in Claim 18 wherein the Lewis acid is chosen from the group consisting of all  
 25 Lewis acids containing boron and magnesium chloride.  
 24. A catalyst as recited in Claim 23 wherein the Lewis acid is tris(pentafluorophenyl)boron.

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